

Sustainable Systems SFA

Research Summaries - 2011

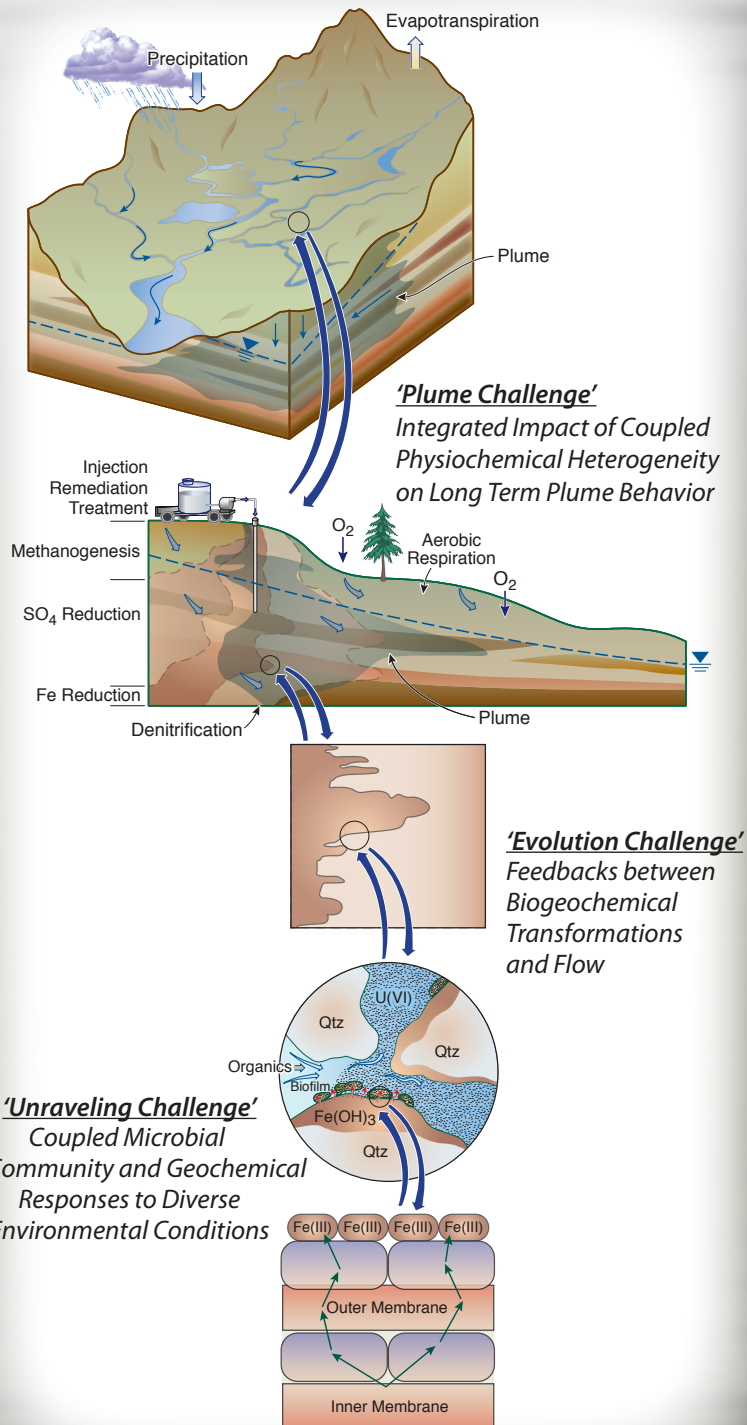


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Sustainable Systems SFA Overview

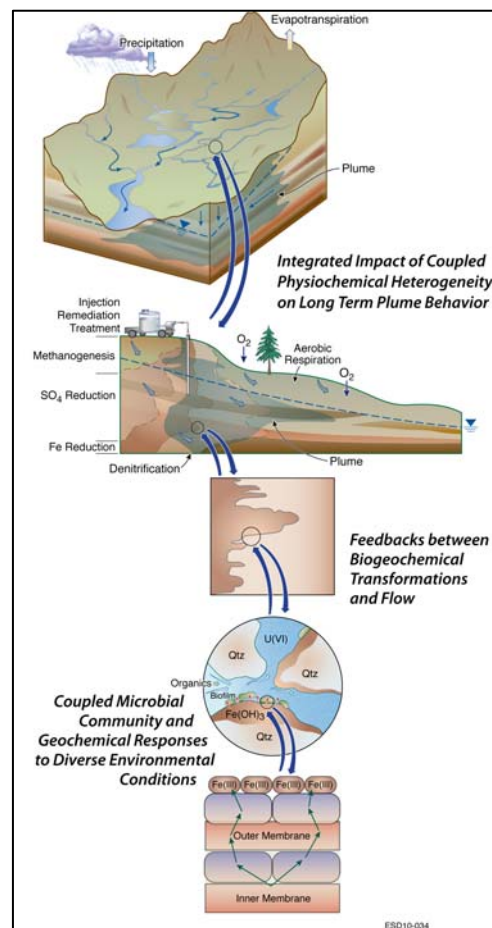
Susan Hubbard

The overarching mission of the Sustainable Systems SFA is to improve the predictive understanding of subsurface flow and transport relevant to metal and radionuclide remediation and long-term environmental stewardship. Developing a predictive understanding of sustainable system behavior is pivotal for effectively implementing sustainable strategies; it represents a major research need facing environmental sciences and is a research challenge relevant to multiple DOE mission areas.

The SFA is organized around three key challenges, in which research teams explore fundamental (hydrological, biological, geochemical) processes, their couplings, and their macroscopic manifestation, as is needed to improve our predictive understanding of flow and transport processes in heterogeneous and hierarchical subsurface systems.

- The “Unraveling Biogeochemical Pathways” Challenge focuses on quantifying critical and interrelated microbial metabolic and geochemical mechanisms, with a key goal to determine if there are diagnostic biomolecular signatures that can be used to inform and constrain reactive transport models. This Challenge focuses on chromium *in situ* reductive immobilization and reoxidation processes, and is being explored at the chromium-contaminated Hanford 100 Site.
- The “Evolution of Pore Structures and Flowpaths” Challenge focuses on developing a predictive understanding of couplings and feedbacks between microbially facilitated biogeochemical transformations and aquifer flow characteristics. This Challenge is aligned with and leverages on field experiments that are being conducted at the uranium-contaminated IFRC Site in Rifle, Colorado.
- The “Predicting Contaminant Mobility at the Plume Scale” Challenge explores the impact of a migrating pH gradient and the use of a “reactive facies” concept as an organizing principle to integrate laboratory and field information about properties and mechanisms, as needed, to make reliable and computationally tractable predictions of U and iodine mobility at the plume scale and over long timeframes. This Challenge is being explored at the Savannah F-Area, where enhanced attenuation is a desired closure strategy.

Complexity, scale transitions, and multidisciplinary are scientific themes that crosscut the Sustainable Systems SFA Challenges. Each challenge uses a hybrid approach, whereby fundamental (hydrological, biological, geochemical) processes and their interactions are explored and diagnostic (or integrative and often macroscopic) signatures of system responses are identified. Scale transitions are considered in each Challenge so that the ensemble of SFA research spans molecular to plume scales. Reactive transport modeling plays an integrative role in the SFA: it allows for transfer of parameters, concepts, and processes across scales, providing a link between the fundamental and system-level research. The SFA investigative approach iterates between laboratory- and field-scale experimentation/observation and hypotheses testing/refinement, all within the context of the reactive transport model and with the goal of improving predictive understanding of subsurface flow and transport.





A Reactive Transport Approach to Understanding Complex, Multi-Scale Subsurface Environmental Systems Overview

INVESTIGATORS: Carl Steefel, Nic Spycher, Eric Sonnenthal, Sergi Molins, Li Li, Mike Kowalsky, Christoph Wanner

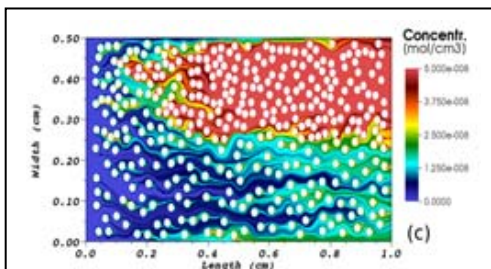
OBJECTIVES: Broadly, the objectives here are to use mechanistic reactive transport modeling to interpret the multi-scale coupled processes that characterize complex subsurface environmental systems. Ultimately, our overarching objective is to develop quantitative predictive models for shallow contaminated systems that can be used for scientifically-based environmental decision making.

APPROACH: Our approach is to develop and apply mechanistic reactive transport models for a variety of subsurface systems over range of scales. To do this, we collaborate closely with other geoscientists collecting and interpreting data using state of the art approaches focused on microbiological signatures, X-ray synchrotron geochemical and geophysical imaging, isotope geochemistry, high resolution geophysics, and hydrologic flow and transport. These diverse scientific approaches provide a remarkably broad set of constraints that can be used to develop and constrain models for the complex subsurface systems, which are in most cases controlled by multiple microbiological, geochemical, and physical processes coupled together in both time and space.

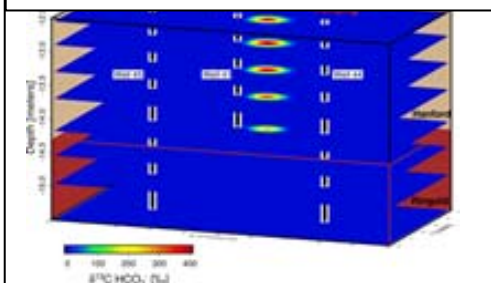
While ultimately the goal is to develop multi-scale (at least pore to catchment scale) models, it is convenient to organize the research making use of reactive transport modeling by the scale of the characterization and simulation. At the individual mineral grain to pore scale, X-ray synchrotron-based microtomography is combined with pore scale reactive transport modeling that is capable of resolving fluid and solid phase compositions and reaction rates at discrete mineral-fluid interfaces and within single pores. To do this, we are developing and applying a new generation of pore scale reactive transport models based largely on direct numerical simulation, with velocity gradients at the pore scale resolved by solving the Navier-Stokes equations for flow.

At the larger scale (>cm), 1D modeling of columns is often used to interpret contaminant behavior under “open system” conditions, that is, as affected by the processes of flow and transport processes similar in concept (if not scale) to field systems. Geophysical, isotopic, and microbiological, and geochemical data at the column scale have been used to constrain the continuum models that average the physical, chemical, and microbiological properties that were discretely resolved in the case of the pore scale models.

Conceptual models and their parameterization developed at the laboratory scale are then used as a starting point for simulations of contaminant transport at the field scale. Further upscaling of continuum parameters may be necessary as a result of the effects of physical and chemical heterogeneity at the field scale.



Simulation of pore scale reactive flow.



Simulation of $\delta^{13}\text{C}$ isotopic ratio one week after Na-lactate injection at Hanford 100H Cr-contaminated site.



Challenge: Unraveling Biogeochemical Reaction Pathways Overview

Harry R. Beller

The **objective** of the "Unraveling" Challenge is to identify and quantify critical and interrelated microbial metabolic and geochemical mechanisms associated with chromium *in situ* reductive immobilization and reoxidation, from the molecular to the local field scale at the Hanford 100 site. Beyond specific application to the Hanford 100 site, we aim to develop tools/approaches that can be used to "unravel" (deconvolute) complex biogeochemical reaction networks.

The following four hypotheses (particularly the first) form the foundation of the Unraveling Challenge:

Hypothesis 1—Microbial processes mediate both direct (enzymatic) and indirect Cr(VI) reduction at Hanford 100H, but indirect pathways dominate sustained reduction.

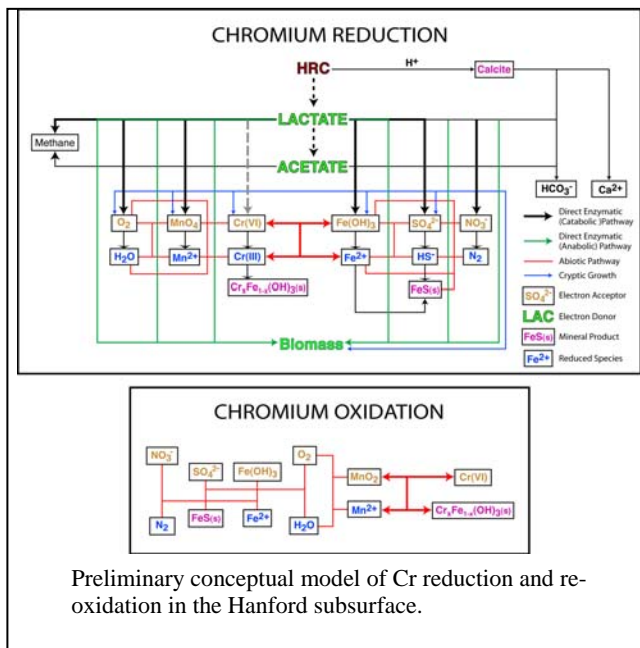
Hypothesis 2—The rate and extent of Cr(III) (re)oxidation will be controlled by the abundance and mineral form of Mn (III/IV) oxides in the sediment.

Hypothesis 3—Fermentative/acetogenic metabolism will promote retention of organic carbon in the aquifer more than respiratory metabolism.

Hypothesis 4—Hydrologic, geochemical, and microbiological interactions between the high-permeability sediments of the Hanford Formation with the underlying, low-permeability sediments of the Ringold Formation result in a redox-stratified aquifer system that has strongly influences Cr mobility.

Tools and approaches used for the Unraveling Challenge are highly interdisciplinary and include: (a) development of "Biomolecular Signatures" (a systems-biology approach [employing metagenomic and meta-transcriptomic sequence data, custom oligonucleotide micorarrays, and quantitative PCR] to identify diagnostic, highly expressed genes in the native microbial community under conditions of interest, and to quantitatively relate expression of these genes to *in situ* metabolic rates); (b) stable isotope biogeochemistry related to Cr and C redox processes; (c) synchrotron-based spectroscopic (X-ray absorption spectroscopy) investigations of biogeochemical processes mediating Cr reductive precipitation; and (d) reactive transport modeling (which uses stoichiometric and mass-balance constraints, isotopic and biomolecular signatures, and hydrological characterization to integrate processes occurring at the pore scale to local field scale).

Experimental systems being investigated for the Unraveling Challenge span a range of scales and include: (a) bacterial isolates (denitrifiers, sulfate reducers, ferric iron reducers, and fermenters) obtained from Hanford groundwater and flow-through column experiments; (b) laboratory microcosms inoculated with Hanford groundwater; (c) laboratory flow-through columns containing Hanford aquifer sediment that simulate a range of conditions relevant to Cr reductive immobilization and re-oxidation; and (d) field biostimulation and push-pull tests (including injection of ¹³C-labeled lactate). Ultimately, the field studies will serve as the proving ground for a predictive, systems-level understanding of Cr biogeochemistry that will be integrated into reactive transport models.





RESEARCH TOPIC TITLE: Using Bacterial Biomolecular Signatures to Interpret Subsurface Biogeochemistry

INVESTIGATORS: Harry R. Beller, Eoin L. Brodie, Ruyang Han, Ulas Karaoz, Hsiao Chien Lim

OBJECTIVE: Our Biomolecular Signatures approach aims to qualitatively and quantitatively assess the metabolic activities of Hanford subsurface microbial communities and their linkage to aquifer geochemical changes that occur during bioremediation. Our primary objective is to determine if there are diagnostic biomolecular signatures indicative of important aquifer biogeochemical processes that can be used to (a) help discriminate between direct (enzymatic) and indirect (abiotic) oxidation-reduction processes relevant to chromium bioremediation and (b) to inform and constrain reactive transport models even when geochemical field measurements do not reveal all relevant processes.

ACCOMPLISHMENTS/FINDINGS: We are using a systems-biology approach to identify diagnostic, highly expressed genes in the native microbial community under conditions of interest and to quantitatively relate expression of these genes to *in situ* metabolic rates. The approach includes two primary components: (a) development of **meta-transcriptome-based gene expression microarrays** and (b) **microbial activity-signature relationships**. Metagenome and meta-transcriptome sequencing have been conducted to support development of custom microarrays for characterizing gene expression in Hanford aquifer microbial communities. The Hanford 100H experimental systems that provided DNA and RNA samples for sequencing include the following: (a) biogeochemical "snapshots" from Hanford microcosms that were inoculated with lactate-amended groundwater and successively passed through denitrifying conditions, sulfate- and Fe(III)-reducing conditions, fermentative conditions, and nitrate-dependent, Fe(II)- and sulfide-oxidizing conditions (Fig. 1); (b) laboratory flow-through columns containing Hanford 100H aquifer sediment and representing denitrifying and fermentative conditions; (c) a time series of groundwater samples taken after biostimulation by lactate injection, and (d) genome sequences of predominant bacteria isolated from denitrifying and fermentative flow-through columns.

For activity-signature relationships, we are using chemostat studies with well-characterized cultures from the Hanford 100H aquifer to determine if quantitative relationships can be found between key metabolic activities and (a) gene copy number (qPCR) and (b) transcript copy number (RT-qPCR) for relevant genes. For example, *Pseudomonas stutzeri* strain RCH2 has been assayed for denitrification (e.g., *narG*, *nirS*) and *Desulfovibrio vulgaris* strain RCH1 has been assayed for sulfate reduction and Cr(VI) reduction (e.g., APS reductase, *dsrA*, cytochrome *c₃*). Strong correlations were found for all genes (e.g., Fig. 2, Han et al. 2010).

2010/2011 PUBLICATIONS:

R. Han, et al., *Environ. Sci. Technol.*, 44:7491 2010

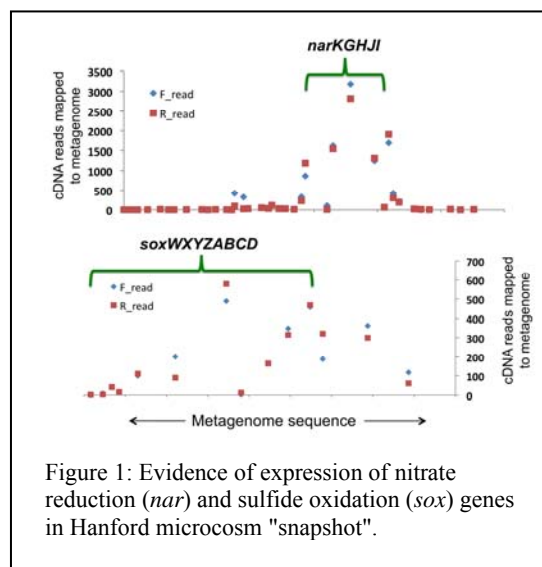


Figure 1: Evidence of expression of nitrate reduction (*nar*) and sulfide oxidation (*sox*) genes in Hanford microcosm "snapshot".

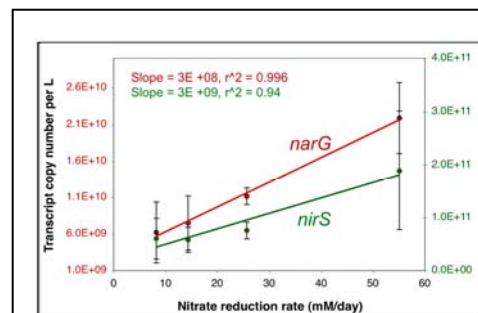


Figure 2: Activity-signature correlations determined for Hanford strain RCH2 and transcripts of diagnostic denitrifying genes.



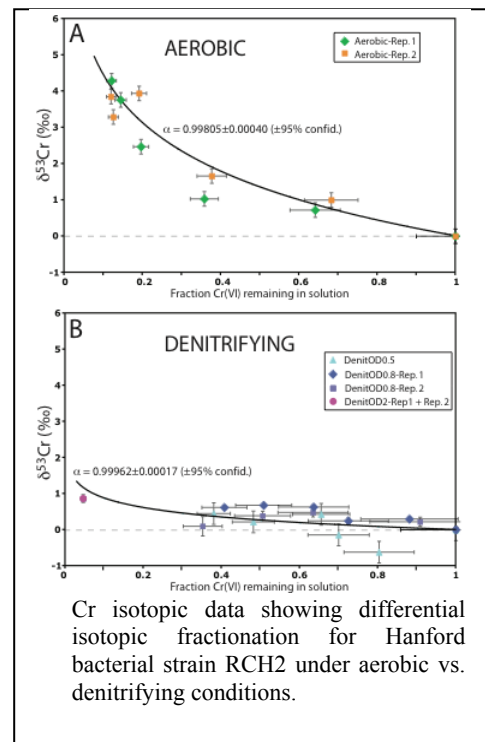
RESEARCH TOPIC TITLE: Isotopic Signatures of Chromium Biogeochemistry

INVESTIGATORS: John N. Christensen, Liping Qin, Ruyang Han, Shaun T. Brown, Li Yang, Boris Faybishenko, Mark E. Conrad, Eric Sonnenthal, Harry R. Beller

OBJECTIVE: It has been shown previously that reduction reactions favor light Cr isotopes, and thus lead to Cr isotopic fractionation. In this work, we are investigating whether diagnostic signatures of stable Cr isotopic fractionation exist that can be used to differentiate among various abiotic and bacterial enzymatic chromate reduction processes/pathways. Such tools would facilitate understanding and modeling of complex Cr biogeochemical behavior in the subsurface.

APPROACH: We have taken a combined laboratory and field approach to characterizing Cr isotopic signatures. In the laboratory, we have used batch-cell-suspension experiments involving bacterial strains isolated from the Hanford 100H aquifer to characterize Cr isotopic fractionation under different electron-accepting conditions. Signatures associated with abiotic Cr(VI) reduction by respiration end-products [such as Fe(II) or sulfide] are being studied as well. We have also measured Cr isotopic fractionation imparted during laboratory incubation of flow-through columns constructed with Hanford 100H aquifer sediment and incubated under various electron-accepting conditions. Finally, we have characterized Cr isotopic signatures in groundwater samples collected after biostimulation of native aquifer microbes by injection of organic electron donors into wells at the Hanford 100H experimental site.

ACCOMPLISHMENTS/FINDINGS: Here we highlight experimental results comparing the Cr isotopic fractionation resulting from reduction by a bacterial isolate (*Pseudomonas stutzeri* strain RCH2) that catalyzes Cr(VI) reduction co-metabolically under both aerobic and denitrifying. Under aerobic conditions, reduction of Cr(VI) by strain RCH2 imposes an isotopic fractionation (ϵ value) of $2.00 \pm 0.4\text{‰}$. In contrast, under denitrifying conditions, the same bacterial strain produces substantially less Cr isotopic fractionation ($\epsilon = 0.4 \pm 0.2\text{‰}$). We suggest that the contrast for strain RCH2 under these two conditions results from differential chromate transport across cellular membranes, where transport is rate limiting under denitrifying conditions. In analogous experiments with a different Hanford bacterium (sulfate-reducing *Desulfovibrio vulgaris* strain RCH1), comparable fractionation was observed for lactate-driven chromate reduction in the presence or absence of sulfate. This suggests that hydrogen sulfide (an end product of sulfate reduction) does not significantly contribute to Cr(VI) reduction by strain RCH1 under these conditions, even though Cr(VI) reduction is somewhat faster in the presence of sulfate. For the column experiments involving Hanford sediments, we have shown that we can derive bulk Cr isotopic fractionation factors that may be diagnostic of the processes involved.



FUTURE DIRECTIONS (2012):

- Column experiments optimized for Cr isotopic measurement of fractionation factors.
- Measurement of Cr isotopic abiotic fractionation by biogenic ferrous iron.
- Characterization of Cr isotopic fractionation during re-oxidation.
- Cr isotopic investigation of Cr precipitates from column experiments.



RESEARCH TOPIC TITLE: Mechanisms of Cr(VI) Reduction as Inferred from Synchrotron Spectroscopy

INVESTIGATORS: Peter S. Nico, Charuleka Varadharajan, Harry R. Beller, Ruyang Han, Eoin L. Brodie, Carl Steefel, Li Yang

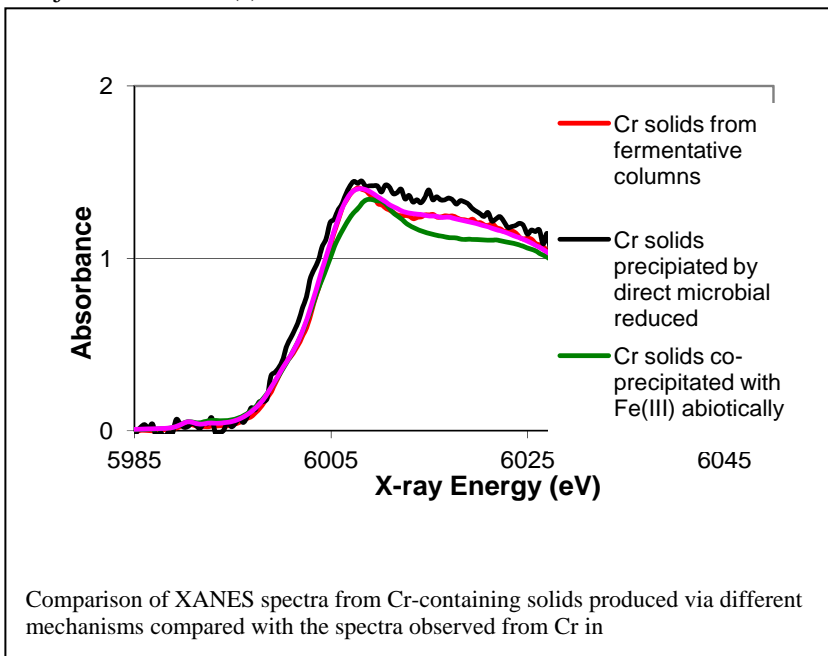
OBJECTIVE: To understand the major mechanism(s) of Cr reduction in Hanford 100H area sediment columns incubated under different electron-accepting conditions.

APPROACH: This laboratory investigation is focused on anaerobic flow-through columns containing Hanford 100H aquifer sediment exposed to synthetic groundwater containing chromate, lactate, and site-relevant electron acceptors (nitrate, sulfate). All columns contained native, bioreducible Fe(III) phases. Chromate in effluent solutions was monitored over time, as were metal cations (ICP-MS) and organic acids (IC). Substantial Cr(VI) reduction occurred in nitrate-amended

(denitrifying) columns and in sulfate-amended columns in which fermentative conditions prevailed. After approximately one year, columns were destructively sampled and the solids analyzed for microbial metagenome and meta-transcriptome sequence, as well as chromium speciation.

ACCOMPLISHMENTS/FINDINGS: Synchrotron X-ray micro-XANES (X-ray absorption near-edge structure) spectroscopy of Cr-containing precipitates revealed a form of Cr in the treated columns that was not observed in the starting material. This Cr was concluded to have been precipitated as a result of biological activity stimulated via the lactate electron donor. Chromium precipitates were always observed to be associated with Fe, but the observed spectra were distinct from abiotically produced $\text{Cr}_{1-x}\text{Fe}_x(\text{OH})_3$ standards. However, the XANES spectra from the column materials showed a high degree of similarity to $\text{Cr}_{1-x}\text{Fe}_x(\text{OH})_3$ materials produced by bacterial isolates from the columns via microbial reduction of Fe(III) to Fe(II) followed by reaction of biogenic Fe(II) with Cr(VI). Based on these results, the mechanism of formation for the observed precipitates is hypothesized to be indirect biological reduction of Cr(VI) via biogenic Fe(II).

FUTURE DIRECTIONS: Before a definitive conclusion can be reached regarding the major mechanism of Cr(VI) reduction, several questions still remain. First, total digestion of column solids must be performed to verify that the majority of reduced Cr was retained within the solid matrix. Second, since the same Cr products were observed under both fermentative and nitrate-reducing conditions, and Fe(III) reduction is thermodynamically less favored than nitrate reduction, it must be determined if there is an alternative mechanism by which the observed solids could have been produced, or be shown that there is sufficient Fe(II) production even under dominant nitrate-reducing conditions to impact the fate of Cr.

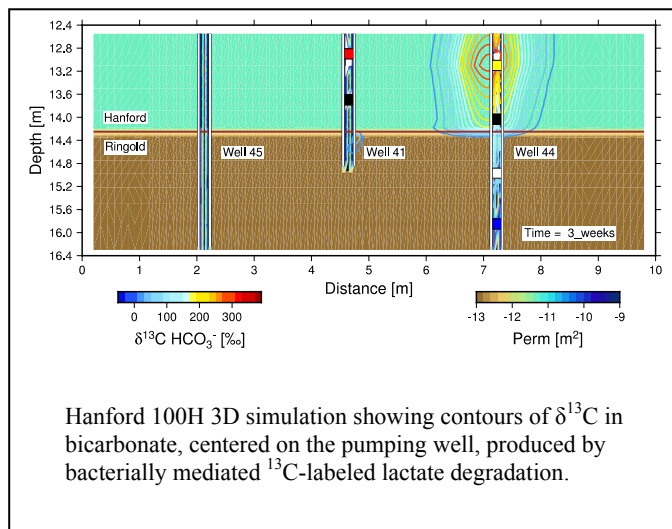




RESEARCH TOPIC TITLE: Reaction-Transport and Isotopic Models for Biogeochemical Processes Accompanying Cr(VI) Reduction

INVESTIGATORS: Eric Sonnenthal, Christoph Wanner, Boris Faybishenko, John Christensen, Mark Conrad, Harry Beller, Markus Bill.

OBJECTIVE: Develop reaction-transport models to investigate and predict reaction pathways associated with microbially mediated Cr reduction and associated biogeochemical processes. Incorporate isotope systematics (e.g., C, Cr, and Sr) into reaction-transport models to help constrain rates of biogeochemical reactions and assess carbon mass balances.



APPROACH: Our approach is to create mechanistic reaction-transport models from the cell- to field scale, incorporating relevant transport mechanisms (fluid flow and diffusion), and bacteria-specific biogeochemical reactions in heterogeneous aquifers; and to introduce thermodynamic and kinetic models to evaluate rates of biogeochemical reactions and associated isotopic systems. At the field-scale, a 3-D model of the Hanford 100H site was developed using higher order gridding, detailed well design, and injection/ pumping/monitoring histories. Models are tested against laboratory and field experiments and used to guide future field tests.

ACCOMPLISHMENTS/FINDINGS: The 3-D model of the Hanford 100H site has successfully captured many aspects of bacterial growth accompanying lactate metabolism, propionate and acetate formation and transport, ^{13}C pathways to bicarbonate, and sulfate reduction. Carbon ($^{13}\text{C}/^{12}\text{C}$) and Sr ($^{87}\text{Sr}/^{86}\text{Sr}$) isotopes were used to independently constrain rates of microbially mediated processes, mixing with groundwater, and calcite dissolution rates. At the cellular and lab experiment scales, Cr ($^{53}\text{Cr}/^{52}\text{Cr}$) isotopic fractionation during microbially mediated and abiotic reduction is controlled predominantly by the rates of reaction, rather than rates of transport or other processes as suggested by several published studies. Two different modeling studies of using novel multiple continuum methods have documented this behavior.

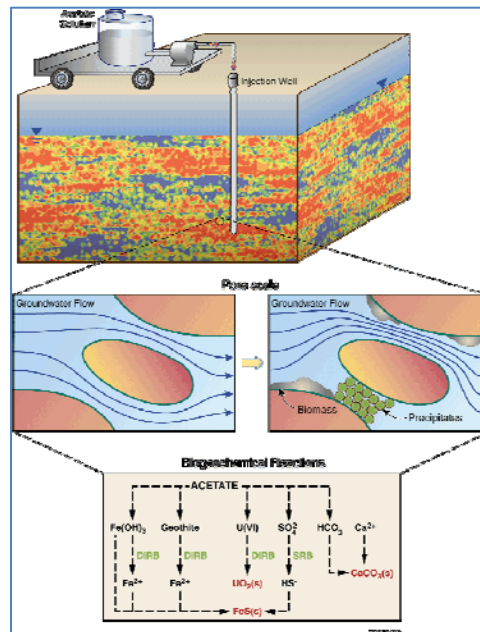
FUTURE DIRECTIONS: We plan to simulate more recent lactate and nitrate injection field tests and complete field-scale Cr reduction and Cr isotopic models. We also plan to incorporate nitrate reduction reactions into biogeochemical models, and to further evaluate mechanisms and rates of Cr(VI) reduction and Cr(III) remobilization in field-scale HRC and lactate injection experiments.



Challenge: Evolution of Pore Structures and Flowpaths

Kenneth H. Williams

The “Evolution of Pore Structures and Flowpaths” Challenge component of the Sustainable Systems SFA focuses on developing a predictive understanding of couplings and feedbacks between microbially facilitated biogeochemical transformations and aquifer flow properties. The Evolution Challenge is aligned with and leverages on field experiments conducted at DOE’s Rifle Integrated Field Research Challenge (IFRC) site in Rifle, Colorado, which seeks to quantify the biogeochemical and hydrological processes that control subsurface uranium mobility and uranium plume persistence. Experimental activities performed as part of both research programs are integrative and complementary, with the Evolution Challenge principally focused on incorporating biogeochemical-hydrological feedback reactions within a modeling framework, through the use of geophysical monitoring, stable isotopes, and estimation approaches.



The Evolution Challenge is organized around three key hypotheses directed toward answering an overarching research question: Is the cumulative impact of pore-scale biogeochemical processes significant enough to impact field-scale flowpaths, which complicate prolonged amendment injection and/or alter conditions favorable for sustainable remediation of contaminated aquifers? The overall objective of the challenge is to quantify reaction-induced, dynamic porosity-permeability relationships in the subsurface, to assess their impact on elemental fluxes and contaminant mobility, and to identify diagnostic signatures of key transformations and feedbacks.

- **Hypothesis 1** - The cumulative impact of biogeochemical transformations will lead to changes in flow characteristics at the field scale that (a) impede delivery of limiting substrates, such as labile forms of organic carbon, and (b) enhance the stability of immobilized, redox-sensitive contaminants, such as uranium.
- **Hypothesis 2** - Biogeochemical reaction rates will exert a key constraint on the spatial extent of hydrological impacts. Kinetically rapid rates will yield pronounced but localized impacts on flow, whereas slower rates will generate spatially extensive, albeit less significant, impacts on flow.
- **Hypothesis 3** - A limited number of critical parameters can be identified that enable accurate modeling of an aquifer's response to a perturbation and its long-term evolution. Integrative diagnostic signatures (biological, geochemical, and geophysical) can be identified that indicate the onset and distribution of these system transitions over field-relevant scales and over a range of time scales.

Like the other two challenges, the Evolution Challenge uses a hybrid approach, in which hydrological, biological, and geochemical processes and their interactions are explored through the use of constrained reactive transport models that integrate them over a continuum of scales ranging from pore to plot (ca. $1\mu\text{m}^3$ to 600m^3). The research approach iterates between laboratory- and field-scale experimentation and observation, with the ultimate goal of improving our predictive understanding of subsurface flow and transport, and the role dynamic processes play in enabling sustainable approaches to contaminant remediation. Research activities performed under the Evolution Challenge and in direct collaboration with the Rifle IFRC research program have yielded approximately 21 manuscripts (published, in revision, or submitted) through January 2012.

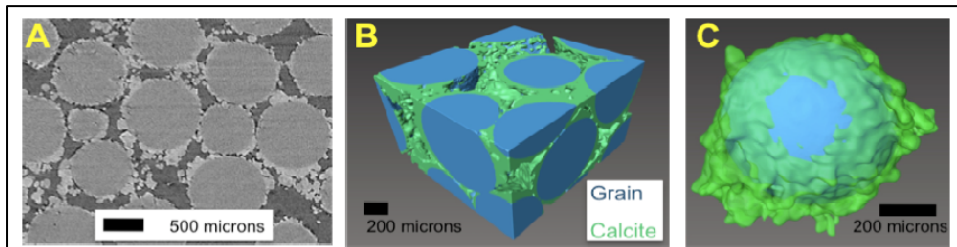


RESEARCH TOPIC TITLE: Dynamic Investigations of Pore-scale Transformations Using X-ray Synchrotron Microtomography

INVESTIGATORS: Jonathan Ajo-Franklin, Peter Nico (assisted by Ryan Armstrong)

OBJECTIVE:

Fundamental to the relationship between dynamic biogeochemical processes and the alteration of permeability, reactive



surface area, and geophysical properties are changes in the 3D micro-architecture of the porous matrix due to precipitation, dissolution, or the generation of secondary semifluid phases (e.g., biofilms). Our research effort explores pore-scale transformations induced by bioremediation at the micron scale using nondestructive synchrotron imaging approaches, primarily x-ray microtomography (CMT).

APPROACH: *In situ* remediation strategies are frequently considered for cleanup of DOE sites. However, the impact of feedbacks between multiscale heterogeneity and induced biogeochemical transformations on remediation efficacy is not well understood. This research task addresses the first hypothesis of the LBNL's SFA *Evolution of Pore Structures and Flowpaths* challenge: that remediation treatments can induce significant enough biogeochemical perturbations to alter pore structures and concomitant macroscopic properties, particularly permeability. To explore the linkage between microstructure alteration and flow processes, we have developed a series of x-ray compatible cells tailored for monitoring biogenic microstructure alteration at the micron scale. These systems have now been deployed at beamline 8.3.2 of the Advanced Light Source to nondestructively monitor the spatial characteristics of both abiotic as well as biogenic CaCO_3 precipitation using CMT.

ACCOMPLISHMENTS/FINDINGS: Micro-column CMT experiments have been conducted to monitor the biogenic clogging process during urea hydrolysis for both pure cultures (*S. pasteurii*) in glass bead packs and natural consortium in aquifer sediment. Both systems show nonclassical precipitate geometries; pure culture experiments in idealized porous media showed rapid clogging (3-orders-of-magnitude reduction in 36 hours) with mixed crystallinity microporous precipitates. In contrast, natural consortium studies with a mixed mineralogy porous matrix showed minimal permeability reduction with highly localized precipitate formation. Related abiotic precipitation studies (not SFA funded) using CaCO_3 seed material showed more traditional precipitate growth patterns. The radically different patterns observed with the same precipitate phase suggest that caution should be used when developing porosity/permeability relationships as part of modeling site response to amendment activity.

FUTURE DIRECTIONS: We are currently working on integrating dynamic microCT imaging with quantitative pore-scale modeling approaches (FD and LB) capable of capturing the aspects of precipitate geometry and distribution crucial in controlling the evolution of permeability.

2010/2011 PUBLICATIONS

- Armstrong, R. et al., 2011, *Geophysical Research Letters*, Vol. 38, No. L08406
- Wu, Y., et al., 2011, *Geochemical Transactions*, Vol. 12, No. 7

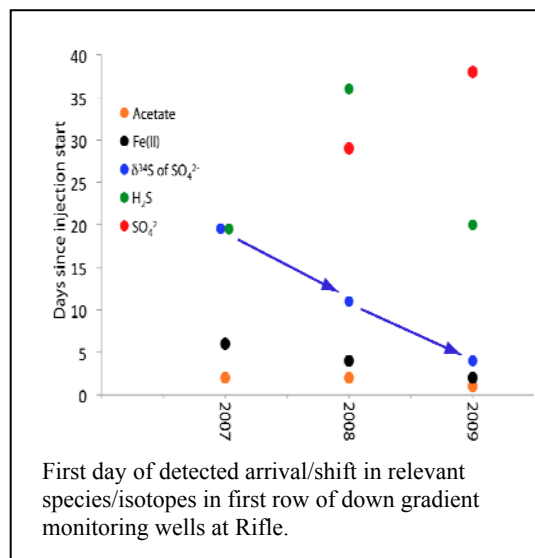


RESEARCH TOPIC TITLE: Stable Isotope Signatures of Bioreduction

INVESTIGATORS: Jennifer Druhan; Markus Bill; Shaun Brown; Mark Conrad; Don DePaolo; Carl Steefel; Ken Williams.

OBJECTIVE: Stable isotope fractionations of key species in the bioreduction process provide information complementary but distinct from traditional concentration measurements. Detection and modeling of such enrichments therefore provide novel constraints on the rates, progress, and secondary mineralization processes associated with *in situ* biostimulation.

APPROACH: At the field scale, stable isotope ratios are measured in fluid samples collected throughout the course of electron-donor amendments. As with variations in major and trace ion concentrations, stable isotope fractionations at the field scale are typically subject to reactive path lengths less than the distance between the injection and first row of monitoring wells. Incorporation of stable isotope fractionations into biogeochemical reactive transport models has thus required development of intermediate or mesoscale column studies designed to operate as direct analogs to field conditions, with the added benefit of sub-20 cm fluid sampling resolution. This combination of field and laboratory datasets has supported adaptation of the CrunchFlow reactive transport model to accommodate both sulfur and calcium isotope fractionations.



ACCOMPLISHMENTS/FINDINGS: At the Rifle field site, sulfur isotope fractionation has been used to constrain the onset of sulfate-reducing conditions (Druhan et al., in review). This technique has been applied to multiple years of electron-donor amendment in a single well gallery, resulting in a previously undocumented trend towards earlier onset of sulfate reduction in subsequent years. In clogged injection wells at the Rifle site, a large enrichment in the stable isotope ratio of aqueous calcium has been documented in association with carbonate precipitation, providing a potentially new means of quantifying secondary mineral precipitation rates. In the laboratory, datasets generated from mesoscale column studies indicate sulfur isotope fractionation is only adequately modeled when the dual Monod equation is used to accommodate the rare isotope through the transition from a zero- to first-order reduction rate. Calcium isotopes show a promising relationship between calcite precipitation (enrichment) and ion exchange (mixing), leading to a ~50 cm zone down-gradient of the electron-donor source in which the fractionation serves as a novel constraint on both rate and exchange coefficients.

FUTURE DIRECTIONS: Based on the field and laboratory datasets generated thus far, we are now adequately prepared to develop a reactive transport model at the field scale that fully incorporates the fractionations of sulfur and calcium as independent parameters. This development will yield new constraints on the timing, rates, and pathways of contaminant remediation.

2010/2011 PUBLICATIONS

- Druhan; Steefel et al., ES&T, *submitted*

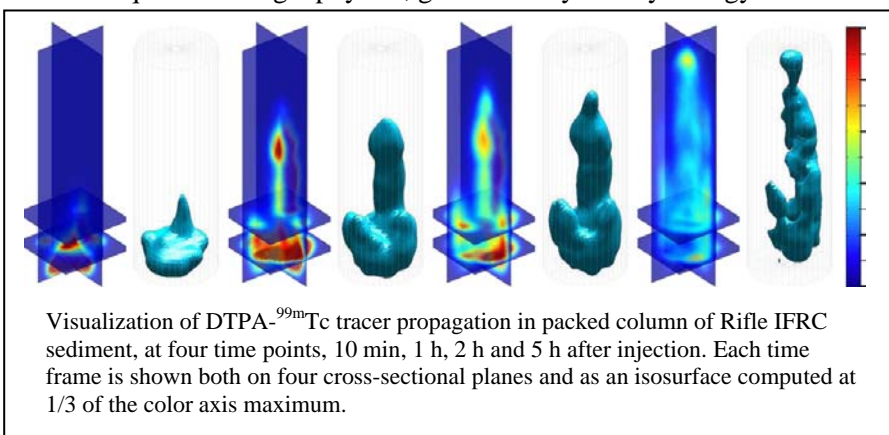


RESEARCH TOPIC TITLE: Non-Invasive Real-Time Imaging of Hydro-Bio-Geochemical Processes

INVESTIGATORS: Peter S. Nico, William W. Moses, Rostyslav Boutchko, Nicholas T. Vandehey, James P. O'Neil, Jennifer L. Druhan, Stefan Finsterle, Aaron Slowey

OBJECTIVE: This collaboration is dedicated to applying tomographic techniques used in nuclear medical imaging to important research questions in geophysics, geochemistry and hydrology research.

APPROACH: The imaging techniques of positron emission tomography (PET) and single-photon-emission computed tomography (SPECT) are well-developed technologies that provide real-time (sec to min) information on the 3D distribution and time-dependent concentration



of gamma- or positron-emitting tracers. The high sensitivity of the technique allows for the use of nonperturbing tracer concentrations (tens of picomoles), allowing repeat investigations of a single system. The spatial resolution (mm to m) fills a mesoscale gap between typical laboratory experiments and field-scale plot experiments. Our approach is to identify and verify radioactive tracers that are sensitive to important properties of subsurface systems, e.g., a conservative tracer for flow paths and a reactive tracer for the presence of Fe(II), then use them to quantitative image the evolution of that property in time.

ACCOMPLISHMENTS/FINDINGS: We have repurposed two commercially available medical tracers ^{99m}TcO₄⁻ and DTPA-^{99m}Tc as an Fe(II) probe and conservative flow tracer, respectively, through vial experiments using biostimulated sediment from the Old Rifle IFRC site. These two tracers then probed the evolving heterogeneity of a 10 cm dia x 30 cm tall column of Old Rifle sediment stimulated with acetate as an electron donor. The images above show the movement of DTPA-Tc in the column and highlight the flowpath heterogeneity in the nominally uniformly packed column. Successive imaging experiments of this column during biostimulation revealed an alteration in flow coincident with the onset of significant sulfate reduction. These data support inverse modeling activities to calculate the evolving porosity and permeability fields within the column as revealed by the changing distribution of tracers.

FUTURE DIRECTIONS: Future work will focus on the development of additional tracers. Potential targets include metabolically distinct groups of microorganisms, e.g., fermenters and metal reducers, calcite precipitation, and alternative conservative tracers. In addition, we anticipate the development of a full-fledged mesoscale experimental facility consisting of a 1–2 m sediment flow cell that can bridge the spatial gap between common column-scale experiments and field-plot experiments, and can be fully instrumented and investigable with our increasing suite of tracers.

2010/2011 PUBLICATIONS

- Boutchko, R., et al., Journal of Applied Geophysics, 2011 (in press)
- Vandehey, N., et al., ES&T, submitted



RESEARCH TOPIC TITLE: Spectral Induced Polarization Signatures of Biogeochemical Transformations at Laboratory and Field Scales

INVESTIGATORS: Yuxin Wu, Kenneth H. Williams, Susan Hubbard

OBJECTIVE: Develop a quantitative and mechanistic understanding of geophysical signatures of multiple, overlapping biogeochemical processes, at laboratory and field scales

APPROACH: The Spectral Induced Polarization (SIP) method is used for this study because of its sensitivity to pore water chemistry, mineralogy, and mineral/water interfacial properties and processes. Lab studies have been used to develop a mechanistic understanding of SIP signatures accompanying biogeochemical transformations, with investigations at the Rifle IFRC site validating the sensitivity of the method under field conditions and over field-relevant dimensions (e.g. 10–100 m²). These studies are incorporated into a complex, system-based approach to quantify (see Chen et al. research highlight) or identify diagnostic geophysical signatures of critical subsurface system transitions, which can then be used for improved field-scale process understanding and to constrain reactive transport models.

ACCOMPLISHMENTS/FINDINGS: Significant progress has been made over the last few years in advancing our understanding of SIP responses to biogeochemical transformations. Examples include:

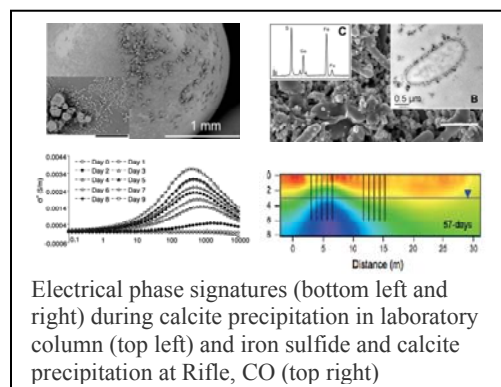
1. SIP signatures of mineral precipitates, including iron sulfide and calcium carbonate (common products of redox fluctuations), have been documented using laboratory column studies, revealing distinct signatures of precipitate formation and particle aggregation.
2. SIP monitoring of stimulated subsurface remediation at the Rifle IFRC site (Colorado, USA) has revealed its sensitivity to system biogeochemical transition over field-relevant scales, revealing the transition from iron reduction to sulfate reduction along surface transects and between boreholes.
3. Sensitivity of SIP to pore fluid chemistry, especially supersaturation of calcium carbonate, has been demonstrated at both laboratory and field scales.

FUTURE DIRECTIONS: Future research will focus on:

1. Advanced understanding of underlying mechanisms linking geophysical signatures with mineral/water interfacial processes critical to reactive transport processes, such as cation exchange.
2. De-convolving SIP signatures associated with fluctuating redox conditions and identification of diagnostic re-oxidation signatures of previously stimulated regions, where multiple mechanisms can affect the aggregate SIP response.
3. Utilizing SIP monitoring data as an additional constraint (e.g., improved spatial localization) for reactive transport models.

2010/2011 PUBLICATIONS

- Williams et al J. Geophys. Res., 115, G00G05, 2010
- Wu et al, J. Geophys. Res., VOL. 115, G00G04, 2010
- Commer et al., Geophysics, 76, 2011
- Flores Orozco et al, J. Geophys. Res., G03001, 2011
- Wu et al, Geochem. Trans., 12:7, 2011



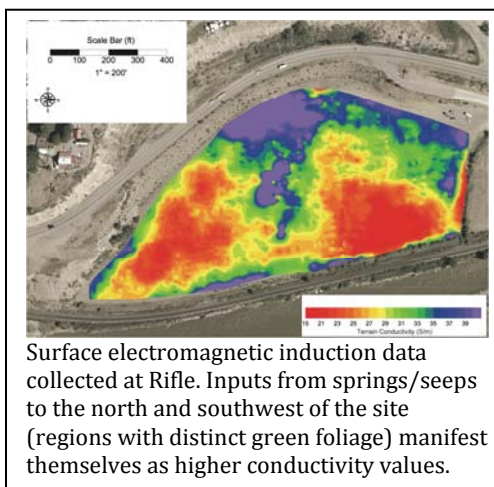


RESEARCH TOPIC TITLE: Natural Rifle System Hydrological, Isotopic, and Geophysical States and Fluxes

INVESTIGATORS: Kenneth H. Williams, Mark Conrad Jennifer Druhan, Craig Ulrich, Baptiste Dafflon, John Peterson, Susan Hubbard

OBJECTIVE: Assemble a comprehensive inventory of geochemical and geophysical data that provides insight into transport processes at the Rifle IFRC site and their relation to surface water–groundwater interactions, aquifer heterogeneity, and uranium (U) plume dynamics.

APPROACH: Acquire a spatially and temporally dense geochemical dataset (δD , $\delta^{18}O$, $\delta^{87}Sr$, $\delta^{34}S-SO_4^{2-}$, $^{234}U/^{238}U$, anions, cations, and inorganic/organic carbon) through bi-weekly/monthly sampling of Rifle groundwater and surface water bounding the site (springs, seeps, and Colorado River). Interpret data within the context of floodplain-scale surface and borehole geophysical measurements, including electromagnetic induction, resistivity, and magnetics data. Through data synthesis, develop a refined floodplain model that accounts for (1) influx of U-bearing groundwater from offsite and (2) the role that magnetic minerals play in impeding natural flushing of U.



ACCOMPLISHMENTS: Analysis of groundwater and surface water samples (Dec. 2010 to Dec. 2011) for δD , $\delta^{18}O$, $\delta^{34}S-SO_4^{2-}$, U, and anion composition has been completed. Preliminary results suggest recharge of the Rifle aquifer occurs primarily through influx of regional groundwater from the north, as evidenced by δD , $\delta^{18}O$, and $\delta^{34}S$ values shared between select surface-water locations and Rifle groundwater. The isotopic composition of Colorado River water is distinct from most groundwater at the site, although seeps to the northeast of the site reflect infiltration from the City of Rifle's discharge lagoons, which receive treated drinking water sourced from the Colorado River. Geochemical data support a sharp water divide between this source term and regional groundwater infiltrating the majority of the Rifle site, with the latter containing naturally elevated levels of U (30–60 ppb). Acquisition and processing of surface electromagnetic (EM) induction and magnetic data has been completed, with EM data suggestive of infiltration of spring/seep water from the north. Magnetic anomalies mapped using a surface gradiometer are corroborated by borehole magnetic susceptibility (MS) data, which reveal an elevated magnetic mineral volume fraction within the capillary fringe. Characterization of alluvial magnetite grains reveals a close association with U, with enrichment up to 150 ppb.

FUTURE DIRECTIONS: Complete geochemical analysis of remaining groundwater and surface-water samples; identify samples of interest for more detailed analysis (e.g., $\delta^{87}Sr$, $^{234}U/^{238}U$). Quantify the role of the magnetic fraction in U sorption/sequestration; use surface and borehole MS data to better delineate the spatial distribution of this fraction within the Rifle aquifer. Acquisition of surface EM and resistivity data at multiple times to assess temporal changes in groundwater inputs from offsite locations (e.g., springs/seeps to north/northeast of site).

2010/2011 PUBLICATIONS:

- Zachara et al., *J Contam Hydrol*, submitted.



RESEARCH TOPIC TITLE: Estimation of Field Redox Status through Geophysical and Geochemical Approaches

INVESTIGATORS: Jinsong Chen, Susan S. Hubbard, Kenneth H. Williams

OBJECTIVE: Many field bioremediation experiments have been carried out at the uranium-contaminated Rifle Integrated Field Research Center (IFRC) site in Rifle, Colorado. The experiments include continuously injecting acetate and bromide for a period of 1 to 3 months and subsequently collecting multiple geochemical samples from downstream monitoring wells. Surface spectral-induced-polarization data have also been collected and used (Chen et al., submitted) to obtain information on the spatial distribution of biogeochemical transformations induced by bioremediation. The biogeochemical reactions vary over space and time as the predominant terminal electron-accepting pathway in the Rifle aquifer transitions from iron to sulfate reduction following introduction of the electron donor (acetate). Developing methods to identify the onset and distribution of these transitions could improve our ability to assess remediation efficacy and sustainability. Our goal is to develop a hidden Markov model to identify key biogeochemical transitions (such as changes in redox state) using time-lapse aqueous geochemical data (such as Fe(II), sulfate, sulfide, acetate, uranium, chloride, and bromide concentrations) and spectral induced polarization data.

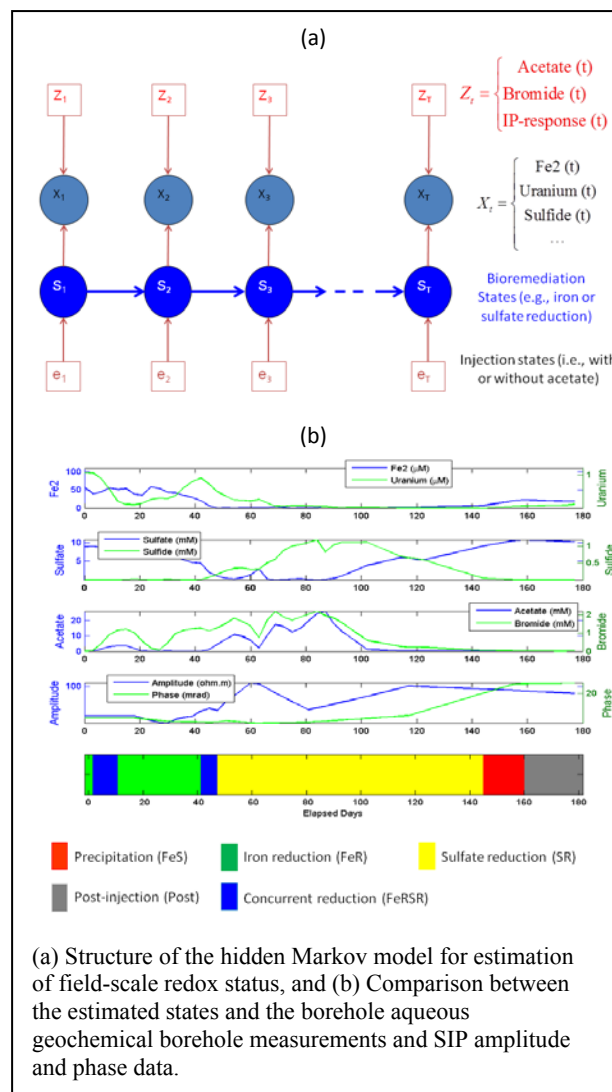
APPROACH: We develop a hidden Markov model with redox status as an unknown state, and multivariate geochemical borehole measurements and surface spectral-induced-polarization data as observations. We define the state-dependent probability distribution according to the recognized main reaction networks and use a multinomial distribution to describe the state transition.

ACCOMPLISHMENTS/FINDINGS: We developed and tested the methodology using a Rifle bioremediation dataset. We find that the developed method allows us to: (1) analyze state-dependent geochemical and geophysical features, (2) estimate state-transition probabilities and identify main state transition sequences following the injection of acetate, and (3) identify key biogeochemical transitions in redox status at wellbore locations using joint measurements.

FUTURE DIRECTIONS: Current studies provide estimation only at the borehole locations. We will combine the current method with a hierarchical Bayesian model to estimate the field-scale redox transitions along a two-dimensional cross section where SIP data are available.

2010/2011 PUBLICATIONS

- Chen et al., *Water Resources Research*, submitted



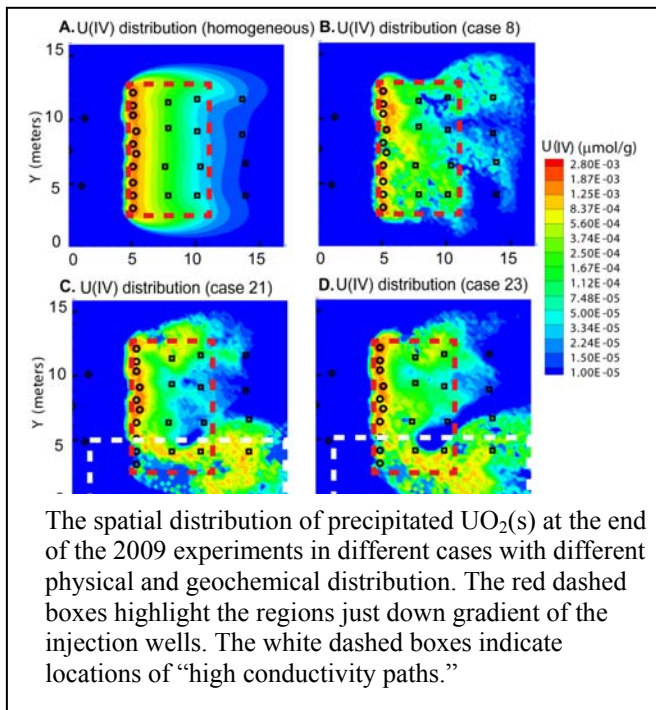


RESEARCH TOPIC TITLE: Influence of Aquifer Heterogeneity on U Bioreduction Processes

INVESTIGATORS: Li Li, Hongfei Wu, Michael B. Kowalsky, Carl I. Steefel, Susan S. Hubbard, Kenneth H. Williams

OBJECTIVE: The goal is to understand and quantify how the spatial distribution of physical and geochemical properties influences biogeochemical processes and U bioreduction rates at the field scale.

APPROACH: The approach integrates field-scale aqueous geochemistry data with multiple modeling schemes, including inverse hydrological modeling, reactive transport modeling, and probability models. After matching field data, the model is used to understand and predict field-scale U bioreduction rates, the accumulation rates of biomass, and the precipitation rates of secondary minerals.



ACCOMPLISHMENTS/FINDINGS:

Our results show that the spatial distribution of hydraulic conductivity and solid-phase minerals ($\text{Fe}(\text{III})$) play a critical role in determining the field-scale bioreduction rates. Due to their dependence on Fe -reducing bacteria, field-scale $\text{U}(\text{VI})$ bioreduction rates were found to be largely controlled by the abundance of $\text{Fe}(\text{III})$ minerals at the vicinity of the injection wells, and by the presence of preferential flow paths connecting injection wells to down gradient $\text{Fe}(\text{III})$ abundant areas. In addition, the amount of biomass accumulation and mineral precipitates are largest in the vicinity of the injection wells, due to the highest concentrations of injected acetate in this area.

FUTURE DIRECTIONS: Future work will aim to integrate geophysical signatures, in addition to aqueous field data, into modeling and quantification of field-scale processes.

2010/2011 PUBLICATIONS

- Li, L. et al., 2011. *Environmental Science & Technology* 45 (23): 9959–9966. doi: 10.1021/es201111y.
- Li, L. et al., 2010. *Journal of Contaminant Hydrology* 112: 45-63. doi: 10.1016/j.jconhyd.2009.10.006.



Challenge: Predicting Contaminant Mobility at the Plume Scale Overview

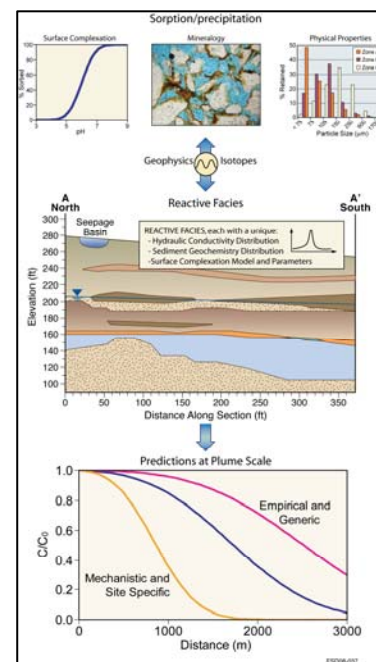
James A. Davis

Predictions of plume evolution, migration, and remediation efficacy at the plume scale often fail because of the simplifying assumptions that are typically made in the representation of heterogeneity, as well as the coupled hydrological and biogeochemical processes taking place within the subsurface. Scientific efforts that focus on predicting contaminant mobility at the plume scale are crucial to guide environmental stewardship, because remedial activities and decisions are based primarily on plume characteristics. This Challenge explores a “reactive facies” concept, as an organizing principle, to integrate laboratory-obtained information about rates and mechanisms with field-based hydrogeological characterization, in order to make reliable and computationally tractable predictions of plume evolution. Progress within this Challenge is expected to impact on one of the major research needs facing the environmental sciences, while also developing scientific strategies relevant to multiple DOE mission areas.

The Plume Challenge is being performed at the Savannah River F-Area, where we focus primarily on uranium and iodine mobility at the plume scale and over long time frames for predictions. Contamination at the site is different from many other DOE uranium-contaminated sites (e.g., Hanford, most UMTRA sites) in that the groundwater plume is acidic in character (pH 3–5), and modeling the migration of pH gradients at the front and trailing edges of the plume is a significant component of the problem, one that is tightly coupled with uranium and iodine mobility. Research in this challenge is developed through tasks specifically designed to explore three hypotheses, using integrated laboratory geochemical, synchrotron, isotopic, geophysical, and reactive transport modeling approaches.

- **HYPOTHESIS 1:** A limited number of sediment groups can be defined that individually display unique U(VI) sorption processes and that adequately represent the spectrum of geochemical behavior in the subsurface when considered as an ensemble.
- **HYPOTHESIS 2:** Reactive transport properties and mechanisms can be represented using a “reactive facies” concept, which capitalizes on the coherent spatial distribution associated with depositional processes and the linkage between hydrological and geochemical properties that often exist in nature.
- **HYPOTHESIS 3:** A scientifically optimal level of field characterization and reactive transport model complexity can be identified for prediction of contaminant mobility at the plume scale, beyond which model accuracy does not increase significantly.

The Plume Challenge research is conducted in collaboration with a parallel effort led by Miles Denham, SRNL, funded by the EM-20 Soil and Groundwater Program. EM further supports geophysical collaborator Rick Miller (KGS), who will collect surface seismic reflection at the F-Area. In addition, we collaborate closely with Jack Istok (Oregon State University) on F-area field push-pull experiments that are evaluating the kinetics and extent of U(VI) desorption/re-adsorption in the contaminated aquifer, under variable chemical conditions. We also work closely with the Advanced Subsurface Computing for Environmental Management (ASCeM) team, which is developing an open-source, high-performance computing environment to guide EM cleanup and closure activities. The Site Applications Thrust Area of ASCeM is using data from the F-Area as part of its ASCeM demonstration project. The following research summaries provide more detail about recent advances associated with the Challenge.





RESEARCH TOPIC TITLE Mechanisms Controlling U(VI) Sorption and Mobility at the F-Area, SRS

INVESTIGATOR(S): J. Wan, W. Dong, T. Tokunaga, P. Fox, J. Davis, H Guo.

OBJECTIVE: The mechanisms controlling U(VI) mobility under acidic conditions common to many DOE waste plumes are poorly understood. Our objective is to understand the relative importance of factors affecting U(VI) sorption under acidic conditions, using the uranium contaminant plume ($\text{pH} < 5$) at the F-Area as a test system.

APPROACH:

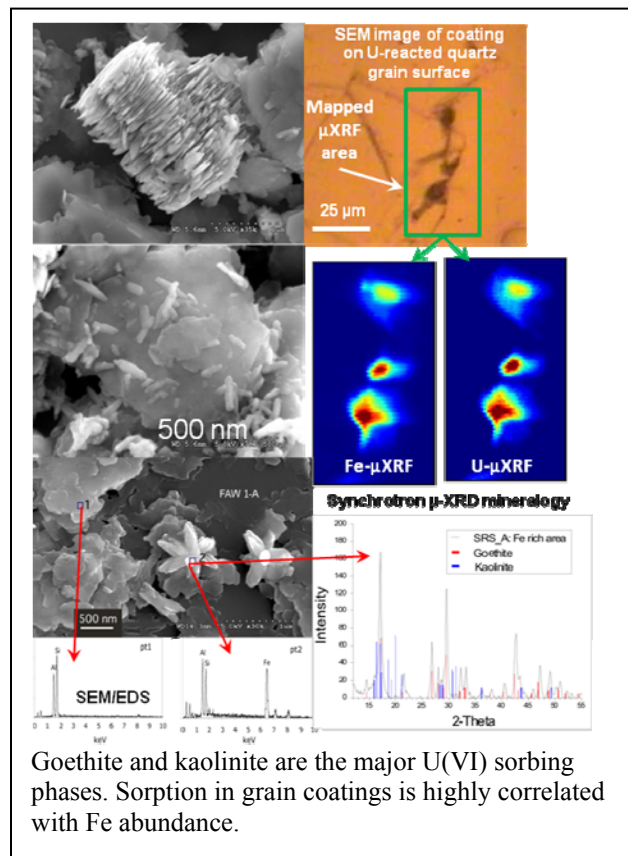
Sediment characterization to identify grain size distribution, mineralogy, surface area, and secondary phases present in grain coatings.

Laboratory batch equilibrium experiments under a range of pH conditions (3.0–9.5), onto different size fractions (bulk, coarse, fine) background and contaminated sediments and reference minerals (goethite, kaolinite) that are the major phases in the sediment fine fraction.

Surface complexation modeling (SCM) to identify the dominant sorption mechanisms and predict U(VI) sorption under variable chemical conditions.

ACCOMPLISHMENTS/FINDINGS:

- A component additivity (CA) SCM model was developed that can predict U(VI) sorption onto background sediments. Application of the model to contaminated sediments, however, results in moderate underestimates of U(VI) sorption at low pH, possibly due to subtle differences in mineralogy between the background and contaminated sediments.
- Goethite and kaolinite were identified as the major sorbents for U(VI) due to their much larger surface area (relative to quartz sand, the mass-based dominant mineral). At $\text{pH} > 4$, U(VI) sorption on goethite predominates, while at $\text{pH} < 4$, kaolinite predominates.
- Surprisingly, the coarse fraction (quartz sand) showed stronger adsorption per unit surface area than goethite and kaolinite under acidic conditions. The explanation for this is still under investigation but may result from higher surface areas (and smaller particle sizes) of iron oxides present in secondary mineral coatings present on quartz sand grains.



FUTURE DIRECTIONS:

- (1) To understand factors and variables controlling U(VI) sorption on contaminated sediments.
- (2) To investigate mineral-water interactions controlling the evolution of plume pH and the impact of decade-long weak acidic conditions on sediment mineralogy.

2010/2011 PUBLICATIONS

W. Dong et al., Environmental Science & Technology, in press.



<u>RESEARCH TOPIC TITLE</u>	Vadose Zone Drainage and Plume Development at F-Area, SRS
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INVESTIGATOR(S): J. Wan, T. Tokunaga, W. Dong, M. Denham, S. Hubbard

OBJECTIVES: The following objectives were pursued in order to fill critical knowledge gaps and provide the basis for understanding plume scale processes.

1. Locate the plume trailing edges.
2. Quantify plume recharge from the source zone, the capped basin vadose zone.
3. Predict plume development: time- and distance-dependent concentrations for *non-reactive contaminants*.

APPROACH:

- To identify plume trailing edges, we constructed 2-D plume geochemical profiles from the edge of the source zone down-gradient along the plume flow path, using data from a limited set of field borehole sediment samples (drilling is costly).
- To estimate vadose zone drainage and predict plume concentrations as functions of time and distance, we developed conceptual and mathematical models, using data from historical disposal records, regional hydrologic records, and 20 years of the Site groundwater monitoring data.

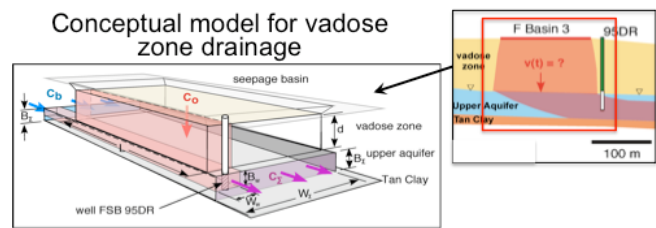
ACCOMPLISHMENTS/FINDINGS:

- The constructed 2-D plume geochemical profiles revealed that the plume trailing edge has emerged for some major contaminants: ^3H , NO_3^- , pH, and U are around 100 meters downstream; and that the plume is still recharged by slow vadose zone drainage, 20 years after the basins were capped.
- A model was developed to estimate time-dependent drainage from the source (vadose) zone, requiring no adjustable parameters. Drainage rates calculated based on ^3H and nitrate are internally consistent.
- A model was developed to calculate concentrations of non-reactive elements, combining vadose zone recharge and dilution based on groundwater flow, rainfall infiltration. The model closely matched 20 years of groundwater monitoring data at three different locations.
- The model predicts that it will take about 10 and 20 more years for NO_3^- and ^3H concentrations, respectively, to decline below their MCLs near the source.

FUTURE DIRECTIONS: The models for vadose zone residual drainage and GW and rainfall dilution are designed for non-reactive elements, but cannot predict behavior of reactive contaminants. The next step is to investigate mechanisms controlling mobility of reactive contaminants including H^+ , U, and ^{129}I .

2010/2011 PUBLICATIONS

- T.K. Tokunaga et al., Vadose Zone J., in review.
- J. Wan et al., ES&T, in review.



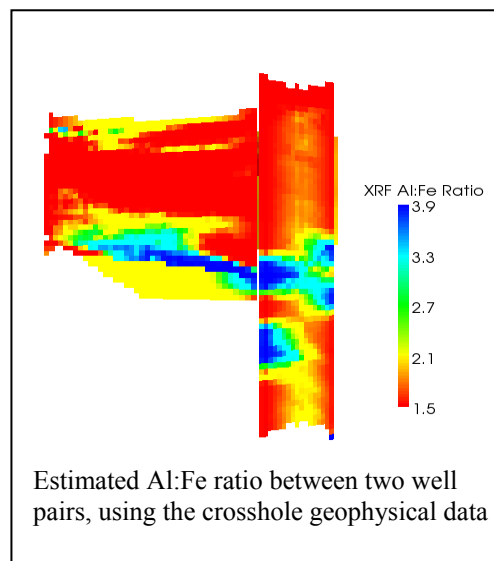
- Drainage rates from Basin 3 can be reliably estimated based on trends in groundwater quality measured immediately down-gradient (FSB-95DR), dilution from background groundwater, and mass balance.
- The groundwater quality even further down-gradient in the plume can be determined by factoring in further dilution from net rainfall infiltration.



RESEARCH TOPIC TITLE: Identifying and Mapping Reactive Facies to Spatially Distribute Reactive Transport Parameters over the Plume Scale

INVESTIGATORS: Haruko Wainwright, Doug Sassen, Jinsong Chen, Susan Hubbard

OBJECTIVE: A central concept of the Plume Challenge is to use reactive facies for tractably describing the subsurface heterogeneity and for improving the predictive capability of long-term plume behavior. Our objectives in this project are (1) to identify the reactive facies that have unique and linked distributions of reactive transport properties (e.g., effective surface area, mineralogy, permeability); (2) to quantify the geophysical signature of each reactive facies type; and (3) to use the spatially extensive geophysical and sparse wellbore data to map reactive facies and associated transport properties over the scale necessary for simulating long-term plume migration. Our study focuses on the Savannah River Site F-Area, contaminated by uranium and other radionuclides.



APPROACH: We used statistical classification/clustering algorithms to identify reactive facies, based on historical and recently collected hydrogeological, geophysical, and geochemical datasets (see Research Summary by Wan et al.). We also estimated the distributions of key reactive transport parameters and geophysical attributes within each reactive facies types. To map the reactive facies over the plume scale, we developed a multiscale Bayesian estimation method to jointly invert wellbore and geophysical datasets in different types, resolution, and spatial coverage.

ACCOMPLISHMENTS/FINDINGS:

- (1) Data mining and iteration with laboratory analysis identified two reactive facies, coincident with the depositional facies: Lagoonal and Beach Barrier. These two have distinct distributions of reactive transport properties: % fines, permeability, and Al:Fe ratio (proxy for kaolinite:goethite ratio).
- (2) The Bayesian assimilation of crosshole radar and seismic data revealed detailed maps of the reactive facies and associated transport properties at the local scale. The surface seismic data, on the other hand, was useful in identifying large-scale heterogeneous structures over the plume scale, such as a unit called Tan Clay Zone, which has a high occurrence of Lagoonal facies.
- (3) Synthetic studies showed that the multiscale Bayesian method can consistently assimilate multitype, multiscale geophysical and wellbore datasets, making it suitable for mapping the reactive facies over the plume scale.

FUTURE DIRECTIONS: The transport simulations will start using the estimated reactive transport properties in high spatial resolution over the plume-relevant scale. They enable us to model flow and transport mechanistically, as well as analyze the value of reactive facies and optimal levels of model complexity for predicting long-term plume behavior. In addition, we are investigating the stationarity of petrophysical relationships used in the current estimation, with a particular focus on exploring how the relationships vary in different aquifers, as well as within and outside of the acidic plume.

2010/2011 PUBLICATIONS

- Sassen et al., Water Resour. Res., submitted



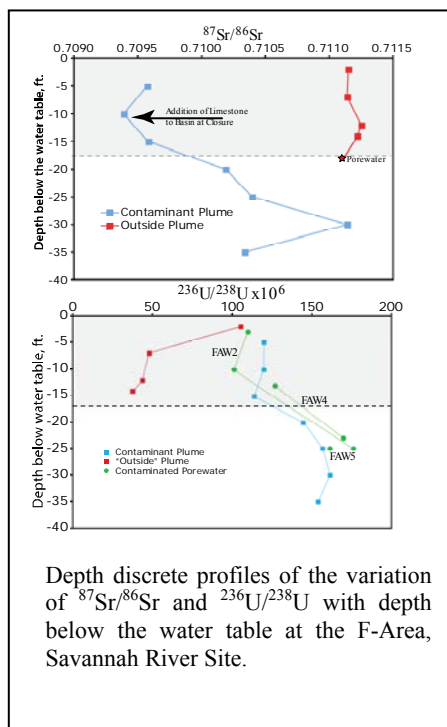
RESEARCH TOPIC TITLE: Determination of Plume History and Evolution with Isotopes

INVESTIGATORS: John N. Christensen, Miles Dunham (SRNL), Mark E. Conrad, Markus Bill, Nic Spycher, James A. Davis

OBJECTIVE: Our objective is to understand the history of contamination and its effect on the structure of the contaminant plume, as well as to quantify and track contaminant mobility. This information then forms a part of the basis for modeling of the evolution of the plume and its fate.

APPROACH: Our approach is to use multiple isotopic systems to investigate contaminant plume history and mobility. As our test location, we use the F-Area situated on the Savannah River Site. Past disposal activities have resulted in a persistent acid contaminant plume, containing ^{90}Sr , U, nitrate, ^{129}I and tritium. For groundwater and pore-water samples, we measure the isotopic compositions of Sr ($^{87}\text{Sr}/^{86}\text{Sr}$), uranium ($^{234}\text{U}/^{238}\text{U}$, $^{235}\text{U}/^{238}\text{U}$, $^{236}\text{U}/^{238}\text{U}$), Nd, as well as the isotopic compositions of water (dD, d ^{18}O) and nitrate (d ^{15}N , d ^{18}O). The isotopic variations reflect natural and anthropogenic processes depending on the element. We use depth discrete water samples as well as conventional monitoring samples to map out the horizontal and vertical spatial variations in isotopic and chemical compositions within the F-Area plume. We also monitor isotopic shifts with time to track the migration of contaminant U and evolution of the plume.

ACCOMPLISHMENTS/FINDINGS: The chemical and isotopic variations in the plume all delineate upper—0–17 ft (0–5m) below the water table—and lower—17–35 ft (5–10m)—zones within the upper aquifer. Together, the data suggest that the lower zone represents the effects of seepage from the basins during disposal operations, while the upper zone represents contamination by infiltration of meteoric water through the sub-basin vadose zone since closure and capping. Through U isotopic analysis, we have been able to detect recent migration as the plume expands laterally, with the greatest extent of U contamination near the top of the aquifer but decreasing with depth. Comparing the U isotopic compositions of groundwater samples collected within the plume two years apart tracks the migration of U from up-gradient portions of the plume. Nd isotopic compositions indicate that high plume rare-earth-element concentrations were controlled by progressive interaction between acid solutions and natural trace minerals in the sediments. Nitrate has an isotopic signature of processed waste, but gives no sign of nitrate bioreduction within the plume.



FUTURE DIRECTIONS:

- Isotopic analysis of depth-discrete porewater samples from recent borings to yield a more detailed cross sections of the plume.
- U and Sr isotopic analyses of push-pull tests (Istok tests) in the F-Area as an *in situ* probe of desorption kinetics.
- U and Sr isotopic analyses of diffusion samplers deployed in F-Area monitoring wells (collaborative with Istok).



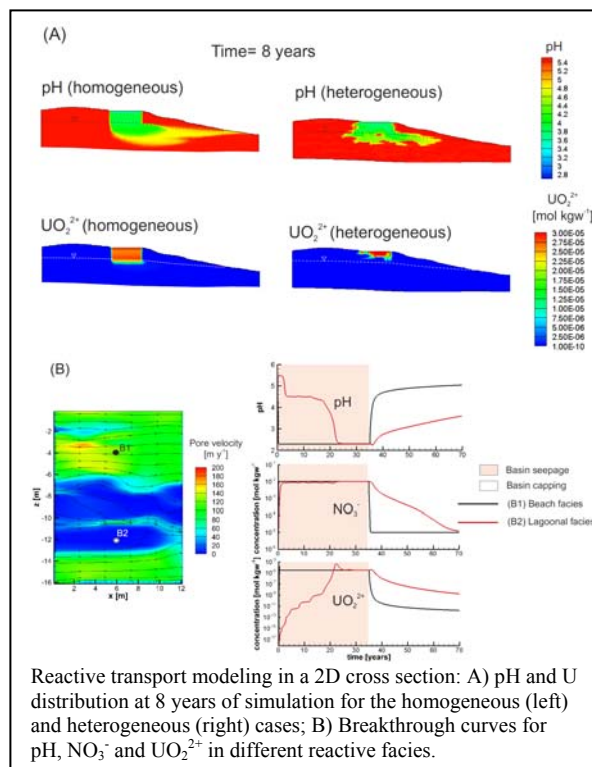
RESEARCH TOPIC TITLE : Reactive Transport Modeling at the Savannah River F-Area

INVESTIGATOR(S): N. Spycher, S. Bea, H. Wainwright, S. Mukhopadhyay, D. Sassen, J. Davis, C. Steefel, S. Hubbard, M. Denham (SNRL), G. Flach (SNRL)

OBJECTIVE: This study aims at understanding key hydrogeochemical processes dictating pH behavior and U transport at the Savannah River F-Area. A nearly 1 km long acidic plume has developed under this site from the disposal of low-level acidic radioactive waste solutions into seepage basins overlying relatively permeable, mostly sandy sediments. The impact of chemical and physical heterogeneities on contaminant mobility is of particular interest. Another goal is to assess the optimal level of model detail needed for reliable predictions of contaminant mobility at plume scales over long time frames.

APPROACH: Horizontal 1D and vertical 2D reactive transport simulations were conducted, including the effects of mineral dissolution and precipitation, as well as H^+ and U(VI) sorption using surface complexation models. Simulations considered the historical 35-year discharge of U-bearing nitric acid solutions, followed by a post-discharge period of 65 years. Physical and chemical heterogeneities were spatially distributed by applying the concept of reactive facies. Modeling was conducted in a step-wise manner, starting with only the saturated zone then increasing complexity by including the vadose zone and a free water table.

ACCOMPLISHMENTS/FINDINGS: Simulations indicate that H^+ sorption reactions on goethite and kaolinite (the main minerals at the site besides quartz), and the precipitation of Al silicates, hydroxides, and/or hydroxy sulfates could delay the pH rebound for decades. Such slow rebound is likely to be exacerbated by residual saturation of the plume below the discharge basins. U concentrations potentially could decrease faster than pH from dilution with clean recharge water. During the discharge period, sorption sites become quickly saturated by the massive H^+ and U influx. Consequently, heterogeneous surface areas (within a given facies) do not affect the simulated historical pattern of the plume, and affect the predicted pH and U transport only at early times and at the plume edges. Therefore, heterogeneities are expected to become relevant over the long term only once contaminant concentrations have decreased below sorption saturation levels. Simulations results are most sensitive to the average surface area of sorbing minerals and to the relative rates of kaolinite dissolution versus acidic influx. Implemented sorption models and parameters also affect model predictions to a lesser extent.



FUTURE DIRECTIONS: The models are being refined to include various conceptualizations of reactive facies and of sorption surface areas. Rigorous uncertainty quantification studies have also been started to further evaluate key model input parameters and their impact on model predictions.

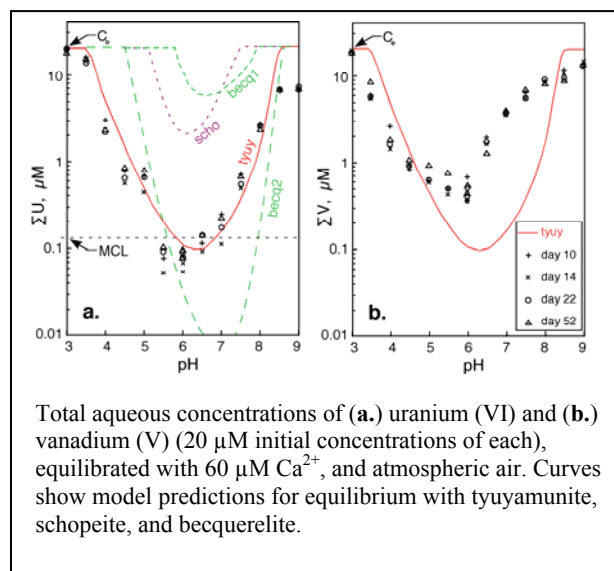


RESEARCH TOPIC TITLE (EXPLORATORY): U(VI) Solids Controlling Aqueous Uranium Concentrations

INVESTIGATORS: Tetsu Tokunaga, Yongman Kim, Jiamin Wan

OBJECTIVE: This project seeks to identify conditions under which U(VI) solids control aqueous U concentrations. This understanding is needed in oxidizing contaminated and natural environments having high levels of total U, where bioreduction is unsustainable. Calcium uranyl vanadate (CaUV) in the form of tyuyamunite, $\text{Ca}(\text{UO}_2)_2\text{V}_2\text{O}_8$, is believed to control U(VI) concentrations in some environments, but reported measurements of its solubility are unavailable in the literature and thus needed. Better understanding is also needed on long-term stability of U(VI) precipitated with phosphate (XUP) versus vanadate (XUV).

APPROACH: Two studies are currently being conducted. In the first, the ability of CaUV to precipitate high concentrations of U is being tested. Batch equilibration experiments are being conducted, with analyses of the aqueous and solid phases. The second ongoing study addresses the problem of U release from vanadate (V) and phosphate (P) solids in contaminated sediments upon equilibration with groundwaters having typical low vanadate and phosphate concentrations. These long-term batch experiments are being conducted in U-contaminated sediments from the Savannah River Site (SR) and the Oak Ridge National Laboratory (OR), providing slightly acidic and slightly alkaline conditions.



ACCOMPLISHMENTS/FINDINGS: Initially high levels of U(VI) were precipitated in CaUV over a range of pH, under oxidizing conditions (equilibrated with air and in the presence of nitrate). Measured U concentrations were in generally good agreement with predictions based on the estimated solubility of tyuyamunite, including the neutral pH range where U is below its MCL. However, analyses of equilibrium vanadate concentrations indicated that tyuyamunite or other CaUV minerals with U:V ratios of 1:1 do not account for all of the U(VI) removal from solution, especially at higher pH. Analyses of the precipitated phase by X-ray diffraction were indicative of very poorly crystalline solids. Nevertheless, these results indicate that a CaUV solid phase can control U concentrations below regulatory goals in the slightly acidic region ($5.5 \leq \text{pH} \leq 6.5$). Comparisons between V- and P-treatments of U-contaminated SR and OR sediments are showing U concentrations remaining below the MCL in both sediments treated with V. However, U concentrations in P-treated sediments are now exceeding the MCL (latest data at 165 days). These results are generally consistent with solubilities of U vanadates versus U phosphates, and demonstrate the importance of testing U stabilization strategies in the limit of equilibrium with background groundwaters.



RESEARCH TOPIC TITLE (EXPLORATORY):

A New Method to Enhance U(VI) Natural Attenuation in Acidic Waste Plumes

INVESTIGATORS: J. Wan, W. Dong, T. K. Tokunaga

OBJECTIVE: Acidic waste plumes containing uranium and other radionuclides are common contaminants in the DOE's legacy weapons facilities. Sustainable remediation/attenuation methods suitable for treating U in acidic waste plumes have yet to be developed. This project is focused on finding a sustainable remediation method for *in situ* immobilization of U(VI) in DOE's acidic waste plumes.

APPROACH:

Humic Acids (HA): Soil HA and Peat HA.

Sorbents: Contaminated sediment samples from the Savannah River Site, and the Oak Ridge Site.

Batch experiments: Kinetics of HA and U(VI) adsorption on the sediments; HA adsorption as function of pH; HA adsorption isotherms; Effects of HA addition on U(VI) adsorption.

Column experiments: "In situ" HA-treatment, followed by leaching with synthetic groundwater

ACCOMPLISHMENTS/FINDINGS:

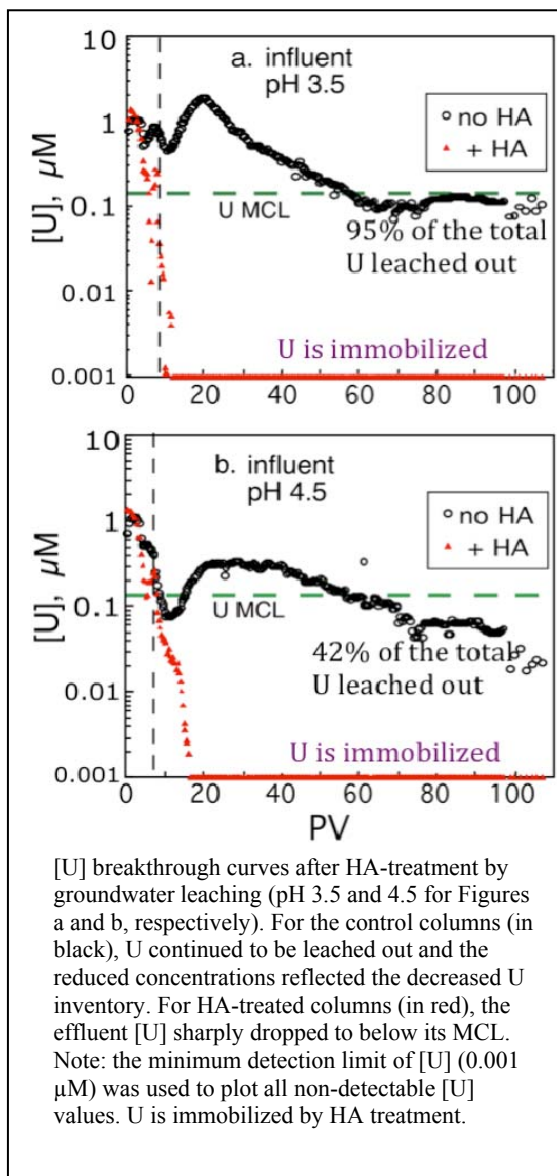
- HA can adsorb onto aquifer sediments rapidly, strongly, and practically irreversibly.
- Adding HA greatly enhanced U adsorption capacity to sediments at pH below 5.0.
- Desorption of U and HA were nondetectable over 100 pore-volumes of leaching with simulated acidic groundwaters.
- Upon HA-treatment, 99% of the contaminant [U] was immobilized at pH < 4.5. HA-treatment is a promising *in situ* remediation method for acidic U waste plumes.
- As a remediation reagent, HAs are resistant to biodegradation, cost effective, nontoxic, and easily introducible to the subsurface.

FUTURE DIRECTIONS:

- We plan to test this method for remediation of iodine (^{129}I) at the F-Area in 2012.
- DOE/EM is considering a field test of this method at the F-Area in 2012.

2010/2011 PUBLICATIONS

- J. Wan et al., Environ. Sci. Technol., 45(6): 2331-7, 2011.





RESEARCH TOPIC TITLE (EXPLORATORY): 3-D imaging of spectral induced polarization data at the Rifle Site

INVESTIGATORS: Michael Commer, Gregory A. Newman, Kenneth H. Williams, Susan S. Hubbard.

OBJECTIVE: Spectral induced polarization (IP) and complex electrical measurements are used in a range of environmental applications to noninvasively estimate important subsurface properties such as the hydraulic permeability in aquifers. The routine 3D interpretation of time-lapse field-scale IP data incorporating complex geology still poses a challenge, mainly due to high computing demands.

APPROACH: We developed a robust and flexible method for the interpretation of IP data, including spectral IP, for environmental field-scale characterization and monitoring purposes. The approach involved adapting a large-scale modeling/imaging framework for frequency-domain controlled-source electromagnetic data that has been used by the oil and gas exploration industry to treat (spectral) IP measurements.

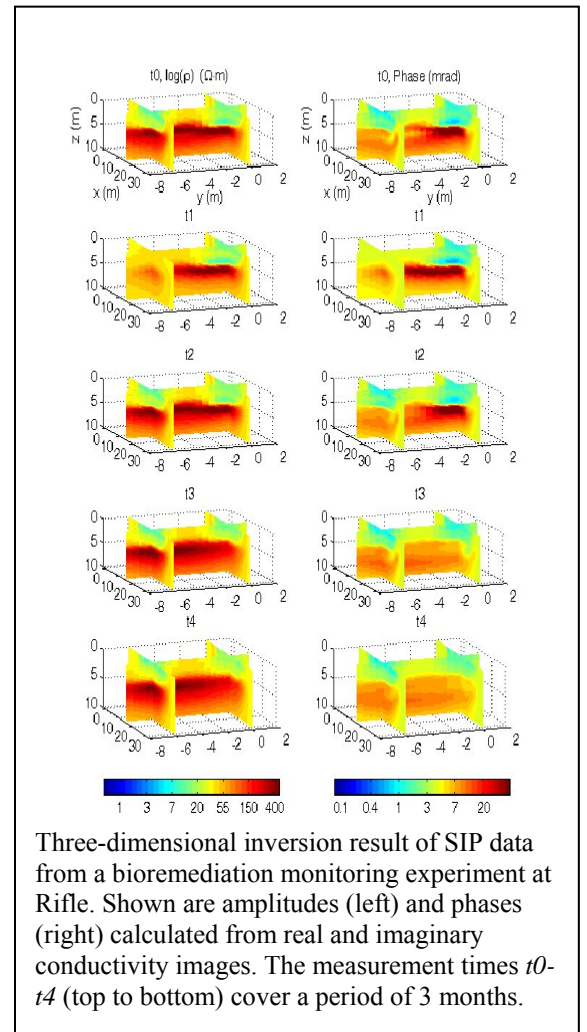
ACCOMPLISHMENTS/FINDINGS: We have enhanced a parallel 3-D EM imaging algorithm to invert for complex electrical conductivity models arising in environmental monitoring studies using IP measurements. The method handles complex subsurface geology and the correction for a common (signal-hiding) problem in IP related to electromagnetic coupling effects.

The monitoring capabilities of the method have been demonstrated on IP data from an environmental remediation experiment at DOE's Integrated Field-Scale Subsurface Research Challenge site at Rifle, CO. Spatiotemporal changes in groundwater Fe(II), which are likely related to elevated levels of subsurface microbial activity, coincided with phase responses derived from inverting time-lapse IP measurements.

FUTURE DIRECTIONS: Future research involves incorporating other geophysical and hydrological data types into induced polarization data inversions for enhanced image appraisal.

2010/2011 PUBLICATIONS:

- Commer M. et al., 2011, Geophysics, 76, F157–F171.





RESEARCH TOPIC TITLE (EXPLORATORY): Pore-Scale Modeling of Biogeochemical Permeability Alteration.

INVESTIGATORS: Dmitriy Silin, Sergi Molins

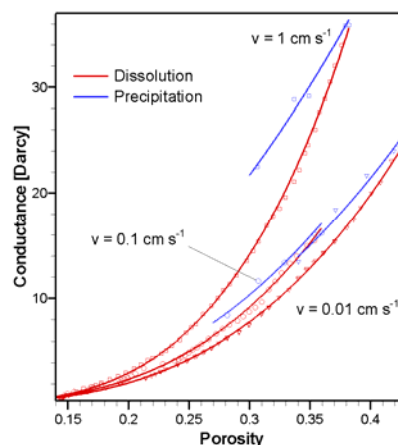
OBJECTIVE: Developing a predictive understanding of couplings and feedbacks between microbially facilitated biogeochemical transformations and aquifer flow characteristics.

APPROACH: We propose a sequential pore-scale model of dynamic coupling between flow and reactive transport. We implement validated geochemical models, including a wide range of reactions relevant to the subsurface systems. Simulations of the pore-space-geometry evolution by CaCO_3 dissolution and precipitation produce porosity-permeability correlations that can be used as input in reservoir-scale simulations.

ACCOMPLISHMENTS/FINDINGS: Permeability modification by mineral precipitation or dissolution can significantly affect injection-well performance in a bioremediation project. Although the size of a cleanup site can be measured in hundreds of meters or even kilometers, the underlying geochemical and hydrologic processes in individual pores eventually define where and how fast the permeability will decline.

Simulations predict that the reduction or enhancement of permeability by precipitation or dissolution develop nonuniformly, concentrating near the inlet boundary. The pore-space evolution is subject to hysteresis if dissolution is followed by precipitation or *vice versa*. Simulations show that the reduction of tortuosity and enhancement of permeability by dissolution are associated with widening and straightening of the pore channels. In precipitation, the declining permeability and increasing tortuosity are associated with narrowing and clogging of the pore throats. Achieving uniform distribution of permeability modification would require a delicate balance between flow and reaction rates, which is complicated by the heterogeneity of natural rock.

FUTURE DIRECTIONS: The model has been validated against a single-pore calcite dissolution experiment by Li et al. (2008). The next steps include model verification using micro-CT data acquired at the ALS, extending the code capability to handle larger micro-CT images of natural rock samples, development of porosity-permeability correlation curves for reservoir-scale simulations, and finalizing the associated manuscript for submission to a peer-reviewed journal.



Hysteresis of porosity-permeability correlation for dissolution (the red curve) and the precipitation (the blue curve) at different flow rates.

